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## BIÊN ĐỘ TÁN XẠ NĂNG LƯỢNG CAO TRONG LÝ THUYẾT HẤP DẪN TUYẾN TÍNH

***Tóm tắt:*** *Dáng điệu tiệm cận của biên độ tán xạ đàn hồi bằng cách trao đổi graviton giữa hai hạt vô hướng ở vùng năng lượng cao và xung lượng truyền cố định được nghiên cứu lại qua phương trình chuẩn thế Logunov-Tavkhelidze trong lý thuyết hấp dẫn tuyến tính. Các bổ chính đối với gần đúng eikonal, bằng cách tiếp cận khai triển gần đúng theo lũy thừa của bậc* $1/p$ *được phát triển, cùng với các đóng góp chính ở vùng năng lượng cao. Biểu thức eikonal của biên độ tán xạ và bổ chính đầu tiên chính thức đã thu được. Thế Yukawa được áp dụng để thảo luận kết quả.*

***Từ khóa:*** *Lý thuyết trường, biên độ tán xạ, gần đúng eikonal.*

# SYNTHESIS, STRUCTURE OF SOME α, β - UNSATURATED KETONES FROM ACETONE AND ALDEHYDES

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***Abstract:*** *Diverse biological activities of α, β- unsaturated ketones such as antibacterial, anti-fungal, weed and insecticide killer, anti-cancer of liver, lung.. have been mentioned in many studies. Otherwise, α,β-unsaturated ketones are derivatives that play a very important role in the synthesis of heterocyclic compounds with very plentiful activity. There have been a number of studies synthesizing [1,2,3,4,5,6,7] and converting them into diverse heterocyclic compounds [8, 9, 10,..] showing the important role of α, β- unsaturated ketones thank to their diverse applications. This paper introduces the synthesis some α, β-unsaturated ketones from acetone and some aldehydes.*

***Keywords:*** *α, β- unsaturated ketones, IR and NMR spectrum, structure.*

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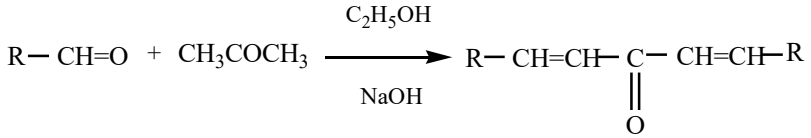
## 1. INTRODUCTION

*Synthesis* α,β-unsaturated ketones are synthesized according to general chemical equations:




*Here: R is hydrocarbon radical.*

The reaction is carried out in an ethanol environment with sodium hydroxide catalyst, the ratio of substances involved (aldehyde/acetone) in the reaction is 2: 1 in moles. After recrystallization, the product is measured for melting point, checked for purity by thin silica gel chromatography in solvent system of n-hexane and ethyl *acetate according to appropriate volume ratio and spectrometry to determine structure.*

## 2. CONTENT

**2.1 Confirm structure of synthesized compounds**

The synthesized substances after measuring the melting point are stable and checked by thin layer chromatography silica gel showing round and neat marks will be determined by modern spectroscopic methods (IR, $^1$H NMR).

***2.1.1. Measuring the melting temperature***

Melting temperature of synthesized compounds was measured on Gallenkamp (UK) at the Organic Chemistry Laboratory, Department of Chemistry, Hanoi National University of Education.

***2.1.2. Measuring IR spectrum***

Infrared spectrum of substances is recorded on PTS-6000 (Bio-Rad, USA) at the Infrared Spectroscopy Room, Institute of Chemistry – Vietnam Academy of Science and Technology, tablet form with solid KBr.

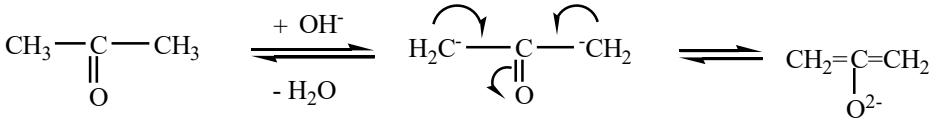
***2.1.3. Measuring nuclear magnetic resonance spectrum***

$^1$H NMR spectrum of substances is measured in solvent DMSO or $CDCl_3$ (TMS is the standard) by Brucker Avance 500 MHz machine at The Nuclear Magnetic Resonance Spectroscopy Room of Chemistry Institute – Vietnam Academy of Science and Technology.

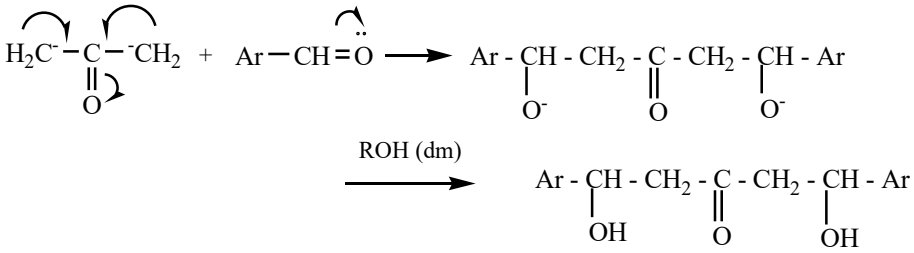
**2.2. Disscuss results**

***2.2.1. Disscuss results of synthesis α,β- unsaturated ketones***

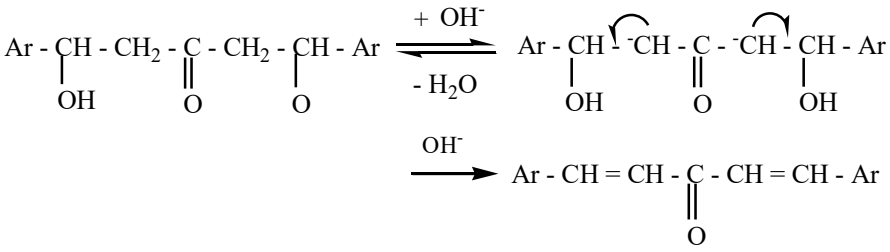
There are many ways to synthesize α, β– unsaturated ketones, but the most common is the aldol – croton condensation reaction. In the synthesis process, the used catalyst used was 20% sodium hydroxide solution. In terms of reaction conditions, we used a simpler, cheaper agent than the previous authors [1; 2; 3] because the authors also closed the cumarin loop before the synthesis of ketones. The α,β– unsaturated ketones are synthesized according [5; 6; 7] with fairly high performance. The reaction went through 2 stages of add-separation as follows [5]: Addition phase: The role of the base in the aldol additive reaction is to activate the methylene component so that it is easily added to the carbonyl group of the aldehyde molecule.




The resulting carbanion attacks the carbonyl group of the aldehydes molecule to form aldol compounds:

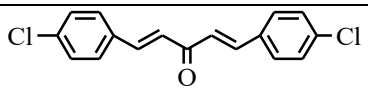
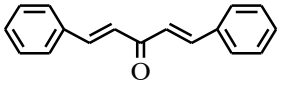
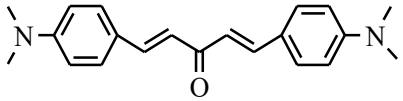
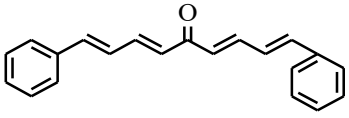


Separation phase: The product of the reaction usually has a trans configuration. The decomposition reaction takes place by E1cb reaction mechanism:



The intermediate product is a carbanion; The less negatively charged carbanion the more stable it is, the higher the efficiency. In the process of synthesizing α, β– unsaturated ketones, we only use one ketone (acetone) so the efficiency and speed of the reaction depend on the aldehyde nature. The higher the density of positive charge on the C atom in the –CHO group of the aldehyde molecule, the easier the reaction will occur. Such substituents having –I, –C effects will increase the positive charge density on the carbon atoms in the –CHO group and vice versa. Reaction performance values are perfectly consistent than expected.

***Table 1. Some physical characteristics of α, β– unsaturated ketones***

| | *α, β–* unsaturated ketones | Some physical characteristics |
|---|---|---|
| A |  | Needle-shaped crystals, light yellow, m.p 196$^0$-196,5$^0$C. Efficiency 73%. |
| B |  | Flake crystals, bright yellow m.p 111 - 112$^0$C. Efficiency 70%. |
| C |  | needle-shaped crystals, dark red; m.p 193 – 193,5$^0$C. Efficiency 65%. |
| D |  | needle-shaped crystals, dark yellow; m.p 148 - 148,5$^0$C. Efficiency 72%. |

Comparing the conditions of synthesis A, B, C, D, we found that: for A, B, D the reaction was easier (at normal temperature) than C (mixed boiling). The reason is that 2 N($CH_3$) groups causes a strong + C effect that reduces the positive charge density on carbon atoms

in the –CHO group of 4-N,N-dimethylaminobenzaldehyde, which reduces the reactivity. This is entirely consistent with the theoretical basis. Synthesized α, β– unsaturated ketones are all crystals, well soluble in solvents DMF, ether, acetone, DMSO, slightly soluble in alcohol and insoluble in water.

### *2.2.2. Research results of molecular structure*

*2.2.2.1. Infrared spectrum (IR) of α, β– unsaturated ketones*

On the infrared spectrum of α, β– unsaturated ketones appear patterned at about 1630–1652 $cm^{-1}$, having a strong intensity, typical for the valence of C = O. The valence band of C = C group (the alkene associated with the aromatic nucleus and the C = O group) and C = C (the aromatic nucleus) in the lower region is about 1572–1600$cm^{-1}$, has a stronger intensity than the C=O. Especially at 980–999$cm^{-1}$ there is a characteristic oscillation for non-flat deformation of vinyl group with trans-configuration when joining into combination with C = O group.

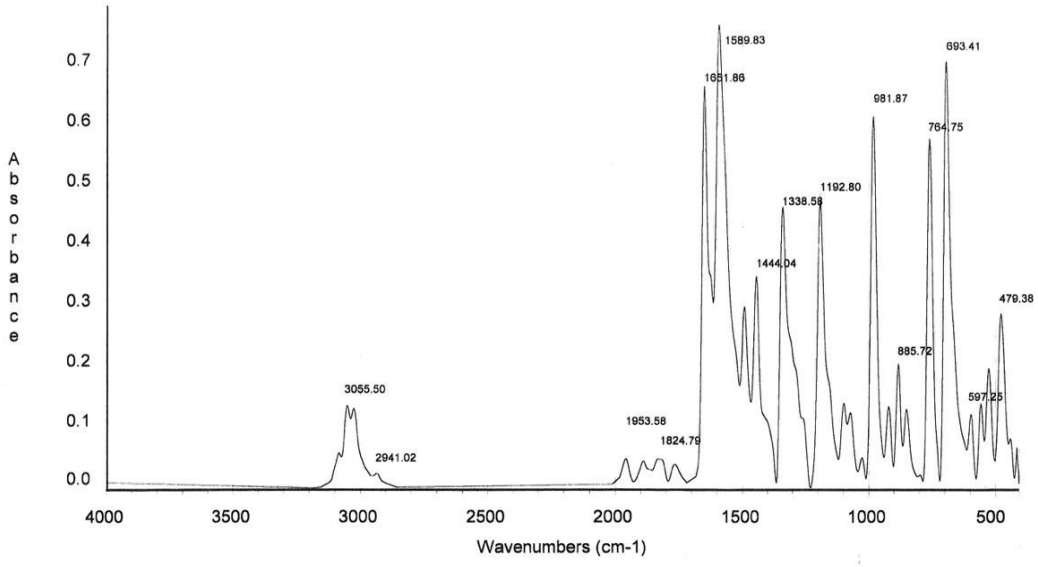



***Fig. 1.*** *Infrared spectrum of compound B*

On the IR spectrum of α, β– unsaturated ketones we find: There was no signals of characteristic valence oscillation of CH bonding of -CHO group ($\nu_{CH\ aldehyde}$ = 2700–2900 $cm^{-1}$, usually show 2 signals, includes one at 2700 $cm^{-1}$). Valence oscillation of C=O group has lower frequency than C=O of initial ketone ($\nu_{C=O\ saturated}$ = 1700-1720 $cm^{-1}$) and aldehydes ($\nu_{C=O}$ = 1680–1715 $cm^{-1}$). Valence oscillation of C=C group has lower frequency but intensity is higher than isolated C=C group ($\nu_{C=C\ isolated}$ = 1620 –1680 $cm^{-1}$). The reason is that the combination of C=O group with C=C group reduces the bonding multiple, so they oscillate at smaller frequencies. Thus, the results obtained when analyzing the IR spectrum

above show that the synthesized α, β– unsaturated ketones are consistent/match with the initial estimates.

***Table 2.*** **Results of IR interpret of α, β– unsaturated ketones (R-CH=CH-)$_2$C=O**

| Kí hiệu | R | $\nu_{CH\ Ar, alkene}$ | $\nu_{CH\ sat.}$ | $\nu_{C=O}$ | $\nu_{C=C, C=N}$ | $\gamma$-CH= (*trans*) |
|---|---|---|---|---|---|---|
| A | 4–$ClC_6H_4$– | 3012,5 | - | 1626,8 | 1586,3 | 982,3 |
| B | $C_6H_5$– | 3055,5 | - | 1651,8 | 1589,8 | 981,8 |
| C | 4–$(CH_3)_2NC_6H_4$– | 2896,3 | 2803,8 | 1636,7 | 1518,2; 1596,3 | 986,4 |
| D | $C_6H_5$–CH=CH– | 3036,4 | - | 1639,9 | 1572,7; 1491,4 | 998,2 |

*2.2.2.2. $^1$H NMR spectrum of α, β– unsaturated ketones*

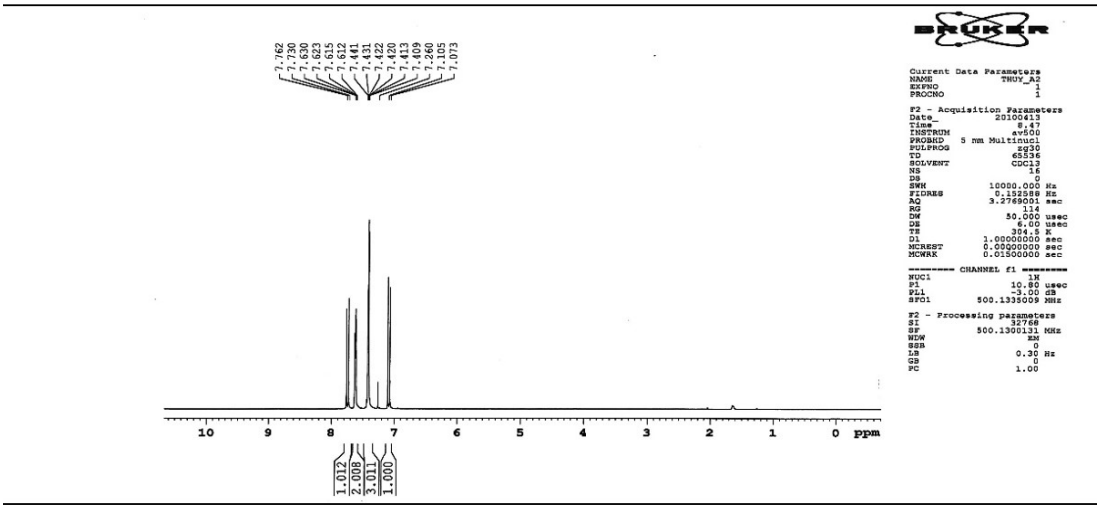


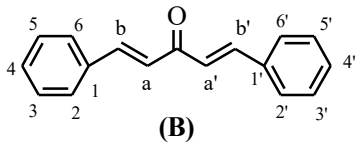
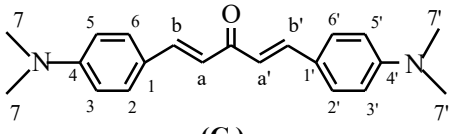

***Fig. 2.*** *$^1$H NMR spectrum of compound B in $CDCl_3$*

On the 1H NMR spectrum of α, β– unsaturated ketones, protons gathered into signal clusters with chemical shift in the range of 6.6 – 7.8 ppm. This is the typical chemical shift for unsaturated protons of = CH– group and there is a pair of doublets in the form of the roof effect in the range of 6.9 – 7.8 ppm with spin – spin interaction constant J = 15 – 16 Hz of group protons –CH = CH– proving that they exist in *trans*-configuration (consistent with IR spectrum). In addition, on the spectrum of compound C, there is also a characteristic signal of $CH_3$–N–Ar group.

Because α, β–unsaturated ketones are symmetric molecules, there are many equivalent protons, moreover, the protons of the benzene ring have quite close displacement in the range of 6.6 – 7.62 ppm. Based on the relative strength, chemical displacement and spin – spin interaction constant, the $^1$H NMR spectrum analysis results of B and C are shown in the following table 3.

*Table 3. Results of $^1H$ NMR interpret of B, C (δ ppm)*

(J (Hz); s: singlet; d: doublet; dd: doublet–doublet; t: triplet; q: quartet; m: multiplet)

| Positions |  **(B)** |  **(C )** |
|---|---|---|
| $H^{a, a'}$ | 7,09; d; 16; 1H | 6,88; d; 15,5; 1H |
| $H^{b, b'}$ | 7,74; d; 16; 1H | 7,68; d; 16; 1H |
| $H^{2, 2'}$; $H^{6, 6'}$ | 7,62; d-d; 6,5; 1,5; 2H | 7,5; d; 9; 2H |
| $H^{3, 3'}$; $H^{5, 5'}$ | 7,41; d-d; 5; 1; 2H | 6,69; d; 8,5; 2H |
| $H^{4, 4'}$ | 7,43; d; 5; 1H | - |
| $H^{7}$, $H^{7'}$ | - | 3,03; s; 3H |

Thus, the results of the above analysis show that: α, β– unsaturated ketones synthesized enough protons as expected. The relative intensity, chemical displacement as well as the spin – spin separation constant of the protons are consistent with the originally expected structure. The results allow proper conclusions about the structure of α, β– unsaturated ketones synthesized.

## 3. CONCLUSION

Four α, β– unsaturated ketones have synthesized from acetone and aldehydes that have not found in references.

The combination of interpret results of IR and $^1H$ NMR spectrums confirmed structure of synthesized compounds.

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